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Modification of Statistical Threading in Two-Component Pseudorotaxane Melts Using the Amphiphilic Approach and Variations in the Confinement Geometry

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Recently we described a coarse-grained model of poly(ethylene oxide) and then employed that model to study the amount of spontaneous threading of cyclic molecules by linear chains in the melt [C. A. Helfer, G. Xu, W. L. Mattice, and C. Pugh, Macromolecules **36**, 10071 (2003)]. Since the amount of statistical threading at equilibrium is small, there is interest in identifying physical changes in the system that will increase the threading. We now use that coarse-grained model to investigate the effect on threading of various hypothetical (but feasible) modifications to the two-component system of macrocycles and linear chains in the melt, and different confinement geometries, that can bring about correlations in the arrangement of the rings. Our work follows on the concept of an amphiphilic approach [C. Pugh, J.-Y. Bae, J. R. Scott, and C. L. Wilkins, Macromolecules **30**, 8139 (1997)] for increasing the statistical threading in homopolyrotaxane melts. We investigate whether introducing such correlations in the macrocycles can increase the spontaneous threading. This paper shows that some of our modifications can yield more than double the amount of threading seen in purely statistical mixing. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1724818]

I. INTRODUCTION

Mechanically interlocked molecules, such as knots, catenanes, and especially rotaxanes, have been of significant interest in recent years,[1–45] due to their potential application as building blocks in artificial molecular machines[33–41] and because they display very different properties from their components.[2,16,43] A rotaxane consists of a linear molecule threaded by one or more macrocyclic rings.[1] The linear chain usually has bulky stoppers at the ends, which prevent the macrocycle from slipping out of the chain. When the bulky stoppers are absent, the macrocycle can slip out of the chain, and such inclusion complexes are called pseudorotaxanes.[40] Although several developments have occurred in the routes for the synthesis of rotaxanes[1–5,17,28–30] and their characterization,[23–27] there have been relatively few computational studies[2,3,31,32] towards understanding the fundamental process of threading in the melt/bulk and the factors that control it. Such studies can contribute substantially to the field by allowing us to increase the yield of threading. Most of the computational work[15–23] has focused on single chain and ring systems. There has also been a growing interest in studying the dynamic properties of rotaxanes systems, e.g., the diffusion of threaded and unthreaded macrocycles,[42] and the shuttling of the macrocycle along the linear chain backbone.[33–40] Simulation in solution has also attracted interest as the conformational characteristics of macrocycles are sensitive to the solvent polarity.[10]

The early theoretical work by Frisch and Wasserman[2] predicted very low yields for the statistical threading of linear chains and macrocycles. The first successful preparation of rotaxanes using statistical methods was achieved by Wasserman,[1] where the yields were close to the predicted low magnitude. Thus it was shown that rotaxanes can be synthesized; however the low yields observed in these and other early studies[3–6] hampered the development of the field. The advent of supramolecular chemistry in the late 1980s afforded higher yields of rotaxanes through self-assembly procedures.[15] In this procedure, a molecular anchor of some kind holds the chain molecule in its threaded position while the bulky stoppers are attached to the ends. Commonly used anchoring methods are based on hydrogen bonding,[24,27,35–37] charge transfer interactions,[17,26,28] and electrostatic interactions[16–18,28] between complementary recognition sites on the ring and the chain. When the chain has two or more recognition sites, the ring can shuttle between the various stations in responses to external stimuli and act as a molecular machine. This type of rearrangement is called ''translation isomerism.'' [16,17] Numerous examples of such machines that are sensitive to photochemical,[34–36] electrochemical,[41] and chemical stimuli[33,39,41] have been reported. However, relatively few studies on the synthesis and characterization of rotaxanes in which both components are made of the same species, and thus do not have any specific binding sites, have been conducted.[1–9,22,31,32]

Our goal in this paper is to study rotaxane formation by statistical methods when the chain and the ring are constructed from the same repeat unit. Such systems have been referred to in the literature as homorotaxanes and homopolyrotaxanes depending on whether the linear chain is short or long enough to thread multiple rings. The synthesis and the factors that can affect the yield in statistical threading such as the ring size, the linear chain length, the temperature, the molar ratios of rings to chains, etc., have been studied by some groups.[1–9] Other groups have applied the statistical

threading method to synthesize several rotaxane systems using polymerization reactions, e.g., polyesters,[11] polystyrene,[12,14] polyacrylate, and poly(methacrylate).[13] However, the synthesis of homorotaxanes or homopolyrotaxanes with satisfactory yields has still proven to be difficult, as the process is purely entropically driven.

Pugh *et al.*[8] proposed a scheme to enhance the threading yield in homopolyrotaxanes by using an amphiphilic approach. Both the macrocycle and the linear chain consisted of poly(ethylene oxide). In this approach, the macrocycle, which is hydrophilic, has an alkyl side chain attached to it. Lamellar or columnar micelles can be generated by dissolving the macrocycles in a solvent that selectively solvates one of its components. If a hydrocarbon solvent is used, the macrocycles should aggregate into reverse micelles due to selective solvation of the hydrophobic side chains. When the PEO linear chains are added to such a system, they will be forced to enter the middle region of the micelle, resulting in increased threading due to higher proximity of linear chains and rings. Moreover, the idea being pursued is that with lamellar or columnar micelles, when one polymer chain threads a macrocycle, it will pass through all similarly aligned neighboring macrocycles and result in higher amount of spontaneous threading.

Recently we have investigated by simulation the factors affecting the statistical threading of linear chains and macrocycles in the melt and in the presence of a solvent.[31,32] A method for detecting threading was presented and it was shown that the appropriate ring size for maximum spontaneous threading of PEO without multiple threading on linear chains is in the neighborhood of $(CH_2CH_2O)_{14}$.[31] Simulation in the presence of solvent[32] showed that a poor solvent gave a higher yield for the threading than a theta or a good solvent. In this paper our goal is to study by simulation additional routes that may be applied as discussed earlier[7–9] to increase the statistical threading in two-component systems where the linear chain and the ring are composed of the same species. Since the synthesis of homopolyrotaxanes is challenging, and few experimental techniques exist for their study, currently computer simulation provides us with the best method to study this conjecture in detail.

We now outline the objectives of the current work in the form of various hypothetical modifications to the linear chain and the macrocycle that are to be tested. We also identify various issues that are of interest in the study of rotaxane systems.

II. OBJECTIVES

A. Hypothesis 1

Covalent attachment of an associating side chain at a single site on the ring should cause the rings to associate. We seek to investigate if the rings can be caused to associate in a geometry that promotes threading. For example, the side chain could be a long aliphatic hydrocarbon. The simplest test for this idea in the simulation does not bother with the complete construction of the tails. Instead we reassign the Lennard-Jones (LJ) parameters for two consecutive beads per ring in a manner that will promote the aggregation of these particular beads.

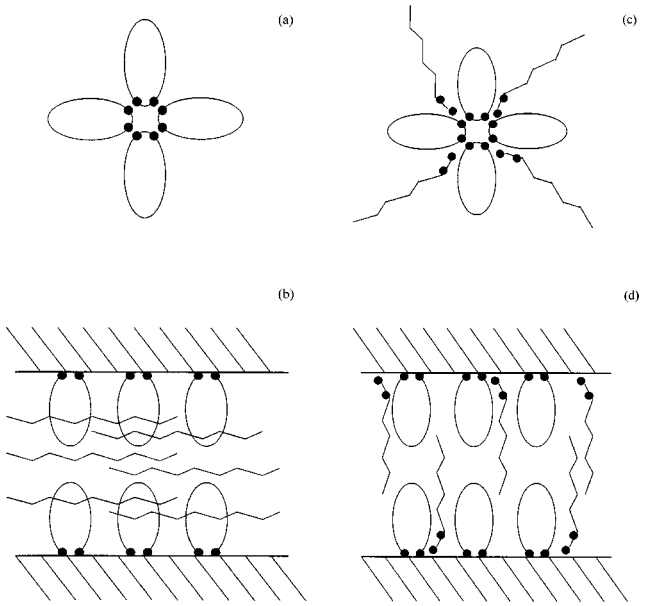

FIG. 1. Sketch of equilibrium configurations of linear chains and rings that might occur under different modifications. (a) **Hypothesis 1:** Modified beads that have attractive interaction among themselves added to the rings. (b) **Hypothesis 2:** Modified beads that have attractive interactions with the surface added on rings. (c) **Hypothesis 3**, Part 1: Modified beads that have attractive interactions among themselves added to rings and linear chains. (d) **Hypothesis 3**, Part 2: Modified beads that have attractive interactions to the surface added on the linear chains and rings.

If water is added to the system as a third component, the hydrocarbon chains will associate. We expect the tails to be in the interior of the aggregate, with the PEO rings in the corona (this structure is opposite of the approach given in Ref. 8). Perhaps the local configuration at the surface should look like the structure shown in Fig. 1(a), which is a cartoon for the segregation of the aliphatic tails (replaced by two modified beads), which produce an alignment of the PEO rings, denoted by an ellipse.

B. Hypothesis 2

Similar to the above, except that we now expose the system to a surface that is net attractive to the modified beads. For example, it might be a surface that interacts poorly with PEO or water, but is neutral or attractive to the hydrocarbon tail. Would this system come closer to supporting the type of aggregate suggested by Fig. 1(b)? Would it facilitate threading? In the simulation the surface is represented by a plane through which the molecules cannot penetrate, and with net attractive interaction with the unique beads in the PEO ring.

C. Hypothesis 3

In conjunction with hypothesis 1 and/or 2, now we assume that the linear chain is not completely PEO but is instead PEO capped at one, or both, ends with a small aliphatic tail. Now the tails tend to seek out the interior of the aggre-

gate (hypothesis 1) or the surface (hypothesis 2). The PEO part of the linear chain happily remains in the corona of the aggregate, or the outer ''brush'' in hypothesis 2. Is the threading enhanced?

III. METHOD AND SIMULATION DETAILS

The Monte Carlo (MC) simulations were performed with coarse grained chains on a high coordination lattice, the 2nnd lattice.[46] The coarse grained chains consisted of mostly PEO molecules[31] with a few beads modified in some cases of our study, such as the end groups. The 2nnd lattice is obtained by eliminating alternate sites from a diamond lattice and contains $10i^2+2$ sites in shell i and an angle of 60° between any two axes. The step length is calculated from the length of the C–C and C–O bonds, l_{CC} and l_{CO}, as $[(8/9)(l_{CC}^2+2l_{CO}^2)]^{1/2}=2.39$ Å. The coarse grained chains can be reverse mapped to their fully atomistic model in continuous space. The simulations were performed using box sizes of varying lengths on the three sides and with or without periodic boundary conditions to represent the presence of the bulk or a solid wall along that direction, respectively. In all cases of study here, the length of the box is reported in terms of the number of lattice sites in that direction.

In each chain, every second atom of PEO is represented by a coarse grained bead. The experimental density of PEO melt at 373 K is achieved with 21% occupancy of sites on the 2nd lattice.[31] This low occupancy facilitates the simulation of larger chains and reduces the equilibration time. The temperature of 373 K is chosen because it is slightly above the melting point of PEO. The ring size, corresponding to $(CH_2CH_2O)_{14}$, is chosen because the probability for threading increases with ring size, and rings larger than this one have a nonzero probability of being simultaneously threaded by more than one linear chain.[31] Therefore selection of $(CH_2CH_2O)_{14}$ optimizes the likelihood that the cyclic component will be threaded by one (and only one) linear chain. The results at equilibrium are not sensitive to the degree of polymerization of the linear chain, because the probability of finding a threaded cyclic molecule at a site along a linear chain is nearly independent of the position on the linear component, i.e., end effects are small for the position of the cyclic component along the linear component.[31] We represent the linear and cyclic components by the same number (21) of coarse-grained beads, but the results should also apply to linear components of larger size. The 50:50 mixture was chosen because this composition optimizes the amount of threading.[31]

Energies: The coarse grained chains are simulated by a Monte Carlo algorithm[46] at 373 K using a Hamiltonian that has two parts. One part is derived from the mapping of the rotational isomeric state model for PEO described by Abe *et al.*[47] onto the coarse grained chains. This part of the Hamiltonian enforces the proper distribution of mean square dimensions for each chain, and for its subchains, through the first- and second-order short-range interactions. The various conformations of the rings are also constrained by the same rotational isomeric state model with the additional requirement of the maintenance of ring closure. The second part of the Hamiltonian incorporates the intermolecular interactions. It uses a discrete version of a continuous Lennard-Jones (LJ) potential energy function, given by the methods introduced by Cho and Mattice.[48] The LJ parameters employed for PEO molecular beads are $\sigma=3.76$ and $\varepsilon/k_B=154$ K. This choice of the discretized LJ potential produces a cohesive system in which the bulk density for a freely standing thin film closely matches the expected density[49] of 1.06 g/cm^3 at 373 K, the temperature of the simulation.[31] Discretization is achieved via the requirement that the continuous LJ function and its discretized counterpart give exactly the same value for the second virial coefficient arising from the pairwise interactions of two particles.[48] Specifically the discretized shell energies, u_i, for PEO beads, at 373 K are 8.113, −0.213, and −0.339 kJ/mol for u_1, u_2, and u_3, respectively.[31] The u_1 is strongly repulsive because the step length on the 2nnd lattice, viz. 2.39 Å, is smaller than the value of σ, 3.76 Å, in the continuous LJ potential. Only the first three shells were used for computational efficiency because although higher shells have attractive energies, the strongest attraction appears in the third shell. The energies of the fourth and fifth shell are negative and much closer to zero than the third shell energy.

TABLE I. Shell energies (kJ/mol) employed for the simulation. (P≡PEO beads, M≡modified beads on linear chains or rings, S≡wall or surface beads.)

Interacting beads	u_1	u_2	u_3
Hypothesis 1			
PP, PM	8.113	−0.213	−0.339
MM	8.113	−0.9	−1.2
Hypothesis 2			
Interacting wall			
PP, MM, PM	8.113	−0.213	−0.339
MS	8.113	−0.9	−1.2
PS	8.113	0.2	0.3
Neutral wall			
All pairs	8.113	−0.213	−0.339
Hypothesis 3			
Same interactions as chosen in hypothesis 1 or 2 above, depending on the absence or presence of the wall, respectively.			

Moves and equilibration: For the study of statistical threading in hypothesis 1 through 3, both single bead moves[50] and pivot moves[51] of 2–6 beads were applied for the equilibration. A Monte Carlo step (MCS) is the length of the simulation that attempts one move, on average, for each bead and each type of move. Therefore, on average, the move of a bead is attempted twice in a single MCS. Moves that cause double occupancy or collapses[50] are disallowed. Collapses occur in configurations of two successive coarse-grained bonds that avoid double occupancy on the 2nnd lattice, but produce double occupancy on the underlying diamond lattice when the missing atoms are restored to the chain or the ring. The system is equilibrated for an average of 6 million MCS using the standard Metropolis criterion[52] for acceptance of moves. The first 3 million steps are discarded and the last 3 million steps are utilized for the calcu-

lations. The length of the simulation was chosen so as to well exceed the equilibration time,[31,32] which is monitored in two ways. First the autocorrelation function of the end-to-end vector of the linear chains $\langle \mathbf{r}(t+t_0)\cdot\mathbf{r}(t_0)\rangle$, goes to zero. Second by making sure that the mean square displacement of the center of mass of both linear chains and the rings well exceeds their mean squared radii of gyration. In the case of hypothesis 2 and 3, we also make sure that the mean square displacement of the center of mass of the rings is much larger than the separation distance between the solid walls. Threading events were determined by the procedure described in detail by Helfer *et al.*[31]

IV. RESULTS AND DISCUSSION

The choices of the interaction parameters for our study are shown in Table I, and the threading results are given in Table II. All the simulations were done at a temperature of 373 K with a system consisting of 40 linear chains and 40 rings, each composed of 21 beads.

A. Hypothesis 1

To test hypothesis 1, two consecutive modified beads (M) were introduced on each macrocycle. Attractive interaction between the modified beads was introduced by making the second and third shell interaction energy (u_2 and u_3) of the MM interaction more negative, as shown in Table I. First shell energy u_1 of MM pair is chosen the same as that between PEO beads. A similar approach of modifying the second and third shell interaction energies was successfully applied previously[32] to simulate good and poor solvent effects on rotaxane systems. In principle, the attractive interactions between the modified beads can also be introduced by choosing a more negative ε for the MM interaction. This approach is needed if we want to simulate the effect of particular beads introduced into the rings. However, for our purpose here, where we only seek to study qualitatively the effect of introducing attractive interactions on the threading content, modification of the second and third shell energies should serve our need.

Helfer *et al.*[31] report that the average number of thread-

TABLE II. Results for the average threading under various hypotheses. *Note*: Box size is given as lattice sites along *x*, *y*, and *z* directions.

Hypothesis 1

Average threading is 1.45. Box size utilized is 20×20×20

Threading relative to melt=0.84

Hypothesis 2

Periodic boundary conditions apply only in the *x* and *y* directions

Interacting wall

Box size	Average threading	Threading relative to melt	Area of overlap from plot (arbitrary units)	Effective area of overlap[a] (arbitrary units)	Normalized ratio of threading yield	Normalized area of overlap[b]
20×20×20	1.43	0.83	8.86	3544	1.0	1.0
24×24×14	2.50	1.45	9.54	5495	1.75	1.55
27×27×11	2.91	1.68	9.29	6772	2.03	1.91
34×34×7	3.73	2.16	6.38	7375	2.61	2.08

Normalization is achieved by dividing the quantity with its value when the wall separation is 20 sites

Neutral wall

Box size	Average threading	Threading relative to melt
27×27×11	1.82	1.05
34×34×7	1.54	0.89

Hypothesis 3

In conjunction with	Box size	Average threading	Threading relative to melt
Hypothesis 1	20×20×20	1.72	0.99
Hypothesis 2	20×20×20	1.96	1.13
	24×24×14	2.34	1.35
	27×27×11	3.21	1.86
	34×34×7	3.14	1.82

[a]The effective area of overlap is obtained by multiplying the area of overlap from a plot with the dimensions of the simulation cell in the *x* and *y* directions. For each wall separation, the dimensions in the *x* and *y* directions change; therefore, the effective area of overlap is relevant for correlation with the threading yield.

[b]The calculation for the normalized area of overlap is based on the effective area of overlap.

ing events for a system of 40 linear chains and 40 rings of 21 beads each is 1.73 ± 0.07 in the melt at 373 K. All four current results are reported as the average number of threading events divided by 1.73. Therefore the results show how the amount of threading is altered by the new situation encountered in each simulation. Each of these dimensionless ratios have an uncertainty of about ± 0.1. With hypothesis 1, we find that the average number of threading events decreases slightly compared to the melt value. The structure the system will likely form is shown in Fig. 1(a), where the rings become associated like a spherical micelle. For the characterization of the structure, the intermolecular pair correlation function (PCF) is appropriate. It gives the probability of finding a particle A at a specific distance from another particle A, normalized by the expectation for this probability if the particles were uniformly distributed in the system. In terms of the high coordination lattice employed in the simulation, the value of the PCF for shell i is defined[53] in Eq. (4.1),

$$g_{\mathrm{AA}}(i) = \langle n_{\mathrm{AA}}(i) \rangle [(10i^2+2)V_{\mathrm{A}}]^{-1}. \tag{4.1}$$

Here $n_{\mathrm{AA}}(i)$ is the number occupancy of A in the ith shell from another A, and V_{A} is the volume fraction of A in the entire system. Since we seek an intermolecular PCF, we ignore pairs of beads that are part of the same molecule. Figure 2(a) depicts $g_{\mathrm{AA}}(i)$ for the modified beads (M), and all of the beads in the rings (R). We find that the intermolecular PCF of the modified beads passes through a strong, broad maximum at shells 2–4, signifying a tendency for intermolecular aggregation. The ratio of the area under the curve from shells 1–3 of the modified beads and the ring beads should roughly indicate the average number of rings that aggregate in the structure, as the attractive interaction for the MM pair only extends up to the third shell. From Fig. 2(a), we find that this ratio is about 2, and thus the structure on average has two associating rings in it. We also performed another simulation using more negative values of u_2 and u_3 for the MM pair viz. -2.13 and -3.39, respectively. In that case, the structure has about nine associating rings in it and the average threading decreases to 0.84. Therefore, the use of more negative values of u_2 and u_3 does not change the qualitative conclusion that this approach does not produce an increase in the amount of threading.

In order to understand this result we investigate whether the linear chain is avoiding the rings. This is achieved by calculating the intermolecular PCF for the linear chains (L), rings (R), and with each other as shown in Fig. 2(b). We find that the L–L PCF is slightly larger than the R–R and L–R PCF in the second and third shell values. Thus the linear chains tend to avoid the rings with the aggregate structure. We conjecture that for the structure shown in Fig. 1(a), the local density in the vicinity of the rings is higher than the average density. Due to this high local density, the linear chain experiences more obstacles as it tries to orient in a threaded geometry through a ring. Moreover, if the same chain has to pass through several associated rings, it will have to adopt a very specific conformation, which is highly improbable given that the threading is purely statistical in nature. In the case of an isolated ring in the melt, the linear chain will have more free space around the ring and thus threading may be comparatively facilitated.

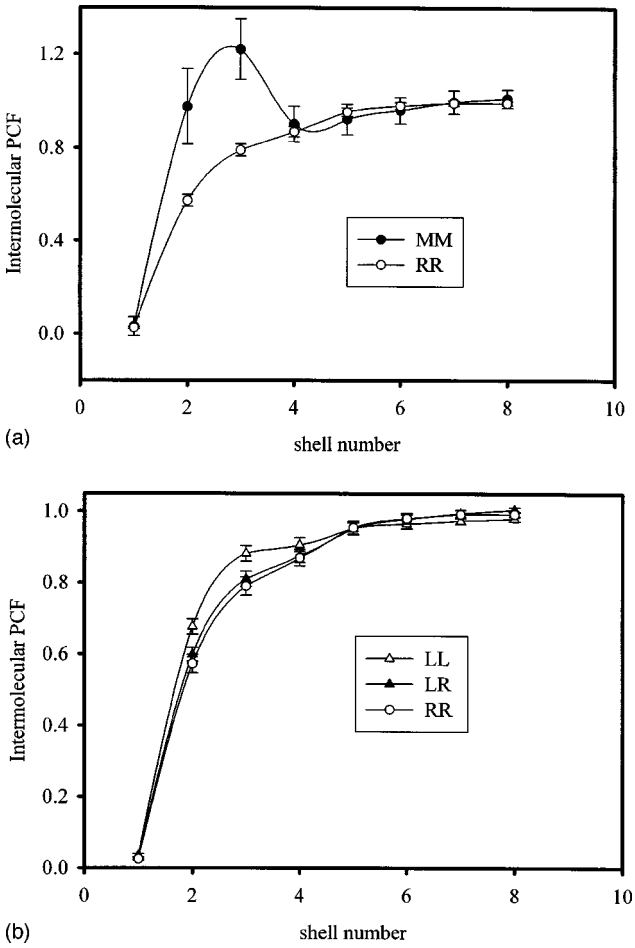

FIG. 2. (a) Intermolecular pair correlation functions (PCF) of the modified beads (M) and all of the beads of the rings (R) for the system used in hypothesis 1. (b) Intermolecular pair correlation functions (PCF) of the linear chains (L), rings (all beads) (R), and each other, for the system used in hypothesis 1. The error bars denote one standard deviation in the average values.

Although the simulations here have been restricted to two-component systems, future study of the system with a third component may be of interest. If the third component was a linear alkane solvent, and if it were present at sufficiently high concentration, there might be a reversal of the structure of the aggregate in Fig. 1(a), with the PEO rings in the core, instead of the corona. The present work with two-component systems cannot examine the extent of threading under those conditions.

B. Hypothesis 2

We investigated the effect of having a surface that is net attractive to the modified beads in the rings. In the process we also found that the average threading is sensitive to the separation distance between the surfaces. The structure the system will likely form is shown in Fig. 1(b). We have impenetrable surfaces along one direction (which in this case is along the z direction) and periodic boundary conditions on the other two directions. The volume of the box is kept ap-

proximately fixed as the wall separation is reduced. The surface is repulsive to PEO and the interaction shell energies for the three types of species are given in Table I. As shown in Table II, the average threading increases as the two surfaces get closer. Although we have not studied the effect of wall separation distance much smaller than the ring size in the simulation, we believe that the maximum statistical threading is obtained when the separation distance is of the order of 2 times the radius of gyration of the ring. The mean square radius of gyration for the rings in this system is 27 ± 3 Å^2. When the wall separation is seven sites, the distance between them along the z direction in Cartesian coordinates is $\approx$13.5 Å. This distance is slightly larger than 2 times the radius of gyration of the rings.

When the surface is attractive to the modified beads, the modified beads remain more or less attached to the surface while the rest of the beads on the ring, being made of PEO, try to stay away from the surface. Thus the ring adopts a configuration somewhat perpendicular to the plane of the surface. The linear chains being completely made of PEO, mostly concentrate at the region in the middle of the two surfaces. As the wall separation decreases, more and more linear chains come in the vicinity of the rings and become threaded, as the plane of the ring is in an ideal geometry when it is perpendicular to the surface and the linear chains are parallel to the surface. In order to understand the structure better, we plot the normalized density of the modified beads, all of the beads in the rings, and all of the beads in the linear chains, as a function of distance from one wall for the system with wall separation$=14$ sites in Fig. 3(a). In this calculation, the polymer beads are put into different bins along the direction perpendicular to the surface and normalized such that a value of 1.0 results if the relative density of the group in each bin is what is expected from the overall density of that group. We find that the normalized density of the modified beads is zero for positions equidistant from the two walls and is very large ($\approx$6–7) near the surface. This implies that the modified beads are indeed attracted to the surfaces and lie close to them. The normalized density of the linear chains show that they remain far from the surfaces and reside mostly near the center region.

It might also be possible to correlate the average threading obtained with the overlap of the areas under the curves of the normalized density for the linear chains and rings. Then the ratios for the threading yields under different wall separations must correlate with the ratios for the areas of overlap. To test this possibility we show a similar plot of the normalized density when the wall separation is 20 sites, in Fig. 3(b). We find that the normalized density of the rings is almost zero at positions equidistant from the two surfaces. Numerical values for overlap areas and effective areas of overlap for each wall separation are also shown in Table II. The effective area of overlap is obtained by multiplying the area of overlap with the dimensions of the simulation cell in the x and y directions, as these change with the wall separation distance. Comparing Figs. 3(a) and 3(b), and the effective area of overlap in Table II, we find that in Fig. 3(a) the effective overlapping area of the linear chains and rings is larger; this results in the larger average threading. In the last two columns of Table II, hypothesis 2, we show the threading content and ratio of effective areas of overlap normalized by their values at wall separation of 20 sites. We find that the two normalized ratios of the threading content and the effective area of overlap agree quite well, except for when the wall separation is seven sites. Thus in general, the threading content can be correlated with the effective area of overlap for the normalized density of the linear chains and rings.

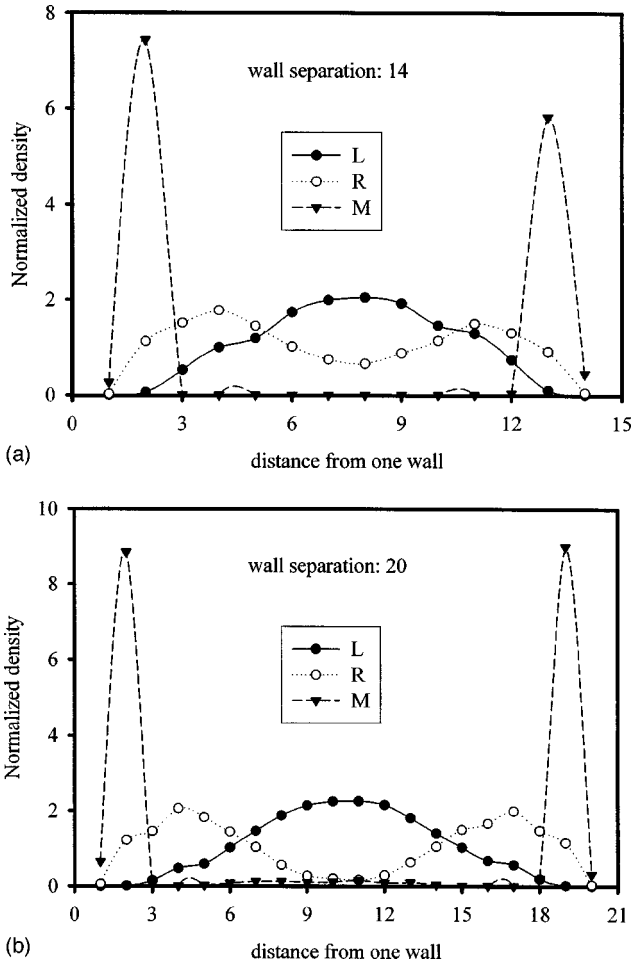

FIG. 3. The normalized density profile for the modified beads (M), rings (all beads) (R), and linear chains (L), as a function of the distance (in 2nnd lattice sites) from one surface, for the system given in hypothesis 2 (a) when the wall separation is 14 sites, and (b) when the wall separation is 20 sites. The normalization is done such that it will give the value of 1.0 if the relative density of the group in each bin is what is expected from the overall density of the group.

However, it is not just the overlapping area that is important in determining the threading content, but also the special relative orientation of the rings and linear chains that produce larger threading events. The overlap area will be large when the surface is neutral too, but in that case the threading will be lower as the rings and linear chains are not in the special geometry as discussed above.

When the wall separation is too small, we believe the rings will collapse and threading will decrease with decreasing wall separation. Unfortunately, we cannot study the effect of very small wall separation, as in that case, most attempts to move the beads of the linear chains or rings along the direction of the solid walls will be rejected. Since we

cannot be sure that the system is truly equilibrated when the separation of the walls is very small, no such results are presented.

To show that the increase in the threading is really due to the attractive interaction of the surface and not due to just the creation of the surfaces, we have performed another simulation where the surface interactions are neutral. In other words, the surface interacts with the modified beads (M) and the polymer beads (P) in the same way as the PEO–PEO interaction. We find that the statistical threading is not enhanced with the neutral interaction. Rather, the average threading is essentially unaffected by the decreasing wall separation; i.e., it is independent of the confinement geometry, whether it is in a bulk or between surfaces.

C. Hypothesis 3

The choice of interactions for testing hypothesis 3 are given in Table I. We postulate that as the modified beads on one end of the linear chain are identical to the modified beads in the ring, they will associate, and the probability that the linear chain will thread the ring will increase.

1. In conjunction with hypothesis 1

The structure the system will likely form is shown in Fig. 1(c). As shown in Table II, the average threading is very close to the value obtained in the melt. Thus in this case the use of modified beads has no effect on the threading.

2. In conjunction with hypothesis 2

The structure the system will likely form is shown in Fig. 1(d). We reverse mapped an equilibrated snapshot of our system in continuous space and verified that indeed the structure of Fig. 1(d) is obtained. In this case the threading is also enhanced compared to the melt value; however, the increment is smaller than that from hypothesis 2 alone. At larger wall separation the increment in threading is larger than the application of hypothesis 2 alone, but at smaller wall separation distance the threading becomes similar to that obtained from hypothesis 2. Thus adding modified beads to the linear chains did not make any substantial difference to the average threading.

V. CONCLUSIONS

We have investigated the statistical threading of PEO linear chains and rings under various geometrical and structural modifications to identify the conditions that can increase threading in the melt. We find that among all of the modifications studied, hypothesis 2 appears to be the most useful as it produces the largest values for the average threading in these two component systems. Hypothesis 3 in conjunction with hypothesis 2 does not improve the results. The essential features of the geometry seen in Fig. 1(b) might be obtained if the walls are replaced by a hydrocarbon fluid of low molecular weight and the modified beads on the rings are replaced by a hydrocarbon tail. Verification of this conjecture by simulation would require study of a three-component system (linear PEO, cyclic PEO, and hydrocarbon). If the three-component system forms a columnar aggregate, the enhancement in threading might be stronger than in Fig. 1(b), where the ''aggregate'' is planar rather than columnar. In the future our goal is to synthesize the modified molecules envisaged here and study their statistical threading through experiments. The present study provides some guidance for methods that will increase the amount of threading, although the best yields in the simulation remain far below the hypothetical limit of 100%. The present results with two-component systems suggest that resort to appropriately constructed three-component systems, and the use of more complex side chains on the cyclic component, might increase the amount of threading if the third component (a selective solvent) and complex side chains work together to produce more well-defined lamellar or columnar micelles of the cyclic component in solution.

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